



## A corollary to the silicic acid leakage hypothesis

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[1] The silicic acid leakage hypothesis (SALH) attempts to explain part of the large and regular atmospheric CO<sub>2</sub> changes over the last glacial-interglacial cycles. It calls for a reduction in the carbonate pump through a growth in diatoms at the expense of coccolithophorids in low-latitude surface waters, driven by a “leakage” of high-Si:N waters from the Southern Ocean. Recent studies that present low opal accumulation rates from the glacial eastern equatorial Pacific have challenged SALH. In a corollary to SALH, we argue that the key to SALH is the dominance of diatoms over coccolithophorids, and this does not depend on the magnitude of diatom production per se. In support of our claim, we show in a numerical model that atmospheric CO<sub>2</sub> can be lowered with even a reduced absolute flux of silicic acid leakage, provided that Si:N in the leakage is elevated and that the excess Si can be used by diatoms to shift the floral composition in their favor.

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### 1. Introduction

[2] Antarctic ice cores record fluctuation in atmospheric CO<sub>2</sub> content that occurred in tandem with global climate change over the past several glacial-interglacial cycles [Petit *et al.*, 1999; Siegenthaler *et al.*, 2005]. Peak glacial CO<sub>2</sub> values are lower than peak interglacial values by 80–100 ppm during the last four cycles and by somewhat smaller amplitudes in earlier cycles. A satisfactory explanation of this fluctuation has eluded us since discovery more than 2 decades ago [Barnola *et al.*, 1987]. As summarized by Archer *et al.* [2000a] and Sigman and Boyle [2000], there are a number of possible mechanisms that have been proposed over the years, but no single one of these is able to explain the full 80–100 ppm amplitude without violating some paleoceanographic constraint. Therefore, a recent move in the field has been to find not a single cause but multiple causes [Archer, 2004], which would be consistent with the fact that it took multiple distinct steps for the global climate to transition from interglacial conditions to glacial conditions.

[3] In 2002, we proposed and demonstrated with numerical models that a reorganization of the global marine silica cycle and associated changes in the carbonate pump could account for a sizable fraction of the 80–100 ppm amplitude [Matsumoto *et al.*, 2002]. With its companion paper [Brzezinski *et al.*, 2002], the proposal has come to be known as the silicic acid leakage hypothesis (SALH). The essential elements of SALH are described below, but in recent years, there has been some effort to verify this hypothesis by trying to test its predictions with paleoceanographic evidence [Beucher *et al.*, 2007; Bradtmiller *et al.*, 2006; Crosta *et al.*, 2007, 2005; Higginson and Altabet, 2004; Kienast *et al.*, 2006]. Among these are “tests” based on opal productivity in the eastern equatorial Pacific that have come out consistently negative.

[4] Here we argue that tests based on opal productivity are significantly weaker than they appear, because SALH is not inconsistent with reduced opal productivity. In a corollary to SALH, we explore this possibility. In the following sections, we review SALH and its recent tests. We then discuss the corollary and demonstrate its effects with a numerical model. Our purpose is to clarify what is and is not SALH. This exercise makes clear what appropriate tests of SALH are.

[5] Today freshly upwelled Antarctic surface waters have approximately 60  $\mu\text{mol kg}^{-1}$  of silicic acid and 25  $\mu\text{mol kg}^{-1}$  of nitrate. These waters support primary production dominated by diatoms that incorporate more silica per unit organic matter than those in most other regions of the world ocean [Brzezinski *et al.*, 2003, 2001; Franck *et al.*, 2000; Pondaven *et al.*, 2000; Smith *et al.*, 2000]. This leads to a net export production across 100 m south of 45°S that has  $\sim 3$  to 4 times more silica per unit organic matter than the rest of the world [Sarmiento *et al.*, 2004]. As some of this upwelled water is advected northward by Ekman transport, Antarctic diatoms continue to preferentially take up silicic acid over nitrate and the export production continues to have high Si:N ratios. This imparts to these surface waters a strong nutrient ratio signal of Si:N < 1. These Antarctic surface waters are therefore relatively replete in nitrate but depleted in silicic acid. This low Si:N signal is then exported from the Southern Ocean to other parts of the world ocean by Antarctic Intermediate Water (AAIW) and Subantarctic Mode Water (SAMW) [Sarmiento *et al.*, 2004]. Diatom production in low-latitude surface waters,

### 2. SALH and Its Corollary

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to which AAIW and SAMW supply nutrients, is likely limited by the low concentrations of silicic acid.

[6] Key to SALH is the observation that an increased availability of iron (Fe) lowers the Si:N uptake ratios by diatoms [Hutchins and Bruland, 1998; Marchetti and Harrison, 2007; Takeda, 1998]. The uptake ratio can drop from as high as 2.7:1 under iron limitation to as low as 1:1 and less with iron addition. The actual export ratio today is higher than the following: of order  $2.7 \pm 0.2$  to  $4.4 \pm 0.2$  across 100 m in the analysis of Sarmiento *et al.* [2004]. As we describe below, the box model that we use in this study uses a ratio of 6 for 250 m deep surface boxes in the Southern Ocean. This is because of a more efficient recycling of organic matter relative to opal dissolution, which drives up the Si:N ratio in the exported material in the so-called silica pump hypothesis of Dugdale *et al.* [1995]. These observations are consistent with the prediction that an increased Fe supply to the glacial Southern Ocean would cause a switch from silicic acid depletion that characterizes today's Southern Ocean to nitrate depletion [Matsumoto *et al.*, 2001]. In other words, Southern Ocean surface waters would turn from today's silicic acid-poor, nitrate-rich to silicic acid-rich, nitrate-poor during the glacial times. The prediction of Matsumoto *et al.* [2001] was made within the context of explaining a northward shift in the opal-rich sediments about the Antarctic Polar Front during the last glacial maximum [Kumar *et al.*, 1995].

[7] In SALH, we called on AAIW and SAMW to transport or "leak" the predicted silicic acid-rich, nitrate-poor Antarctic surface waters during glacial times to the low latitudes [Brzezinski *et al.*, 2002; Matsumoto *et al.*, 2002]. Brzezinski *et al.* [2002] presented sedimentary  $\delta^{30}\text{Si}$  evidence from the Antarctic in support of the predicted switch over the past few glacial-interglacial cycles, and Matsumoto *et al.* [2002] modeled possible changes in phytoplankton community composition and atmospheric  $\text{CO}_2$  content as a result of silicic acid leakage. SALH hypothesizes that silicic acid leakage would enhance diatom production at the expense of other phytoplankton including coccolithophorids, which make  $\text{CaCO}_3$  shells. A reduced production and therefore vertical transport of  $\text{CaCO}_3$  shells imply a weakened carbonate pump [Volk and Hoffert, 1985]. It is this weakening that would cause a lowering of atmospheric  $\text{CO}_2$  content.

[8] A straight forward interpretation of SALH would seem to predict an enhanced, absolute production of diatoms and sedimentary opal accumulation in the low latitudes during times of silicic acid leakage. A number of recent studies have tried to test this prediction, because changes in opal accumulation rate can be determined by paleoceanographic means. Normalization of sedimentation rate by the activity of thorium isotope  $^{230}\text{Th}$  can account for lateral redistribution of sediments by deep sea currents [Bacon, 1984]. Also, the combination of  $^{230}\text{Th}$  with a protactinium isotope  $^{231}\text{Pa}$  in the form of  $^{231}\text{Pa}/^{230}\text{Th}$  ratio is suggested to reflect opal/ $\text{CaCO}_3$  ratio in particulate matter [Chase *et al.*, 2002]. In reality though, complications make sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratio more a qualitative proxy of opal flux than particle composition (R. F. Anderson, personal communication, 2007). Here we simply accept at face value

the assumption that sedimentary opal accumulation rates quantitatively reflect opal production at the surface.

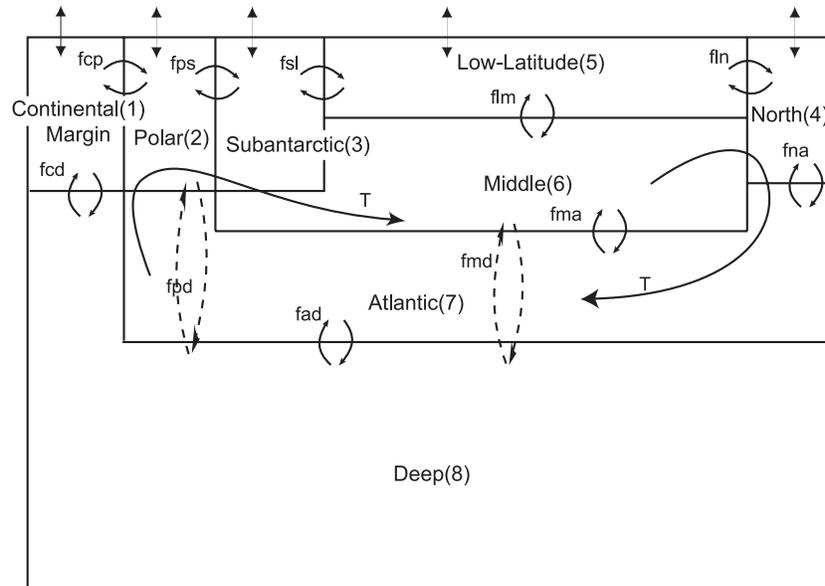
[9] Available estimates of opal accumulation in the eastern equatorial Pacific based on  $^{231}\text{Pa}/^{230}\text{Th}$  ratios and  $^{230}\text{Th}$  normalization consistently indicate lower opal accumulation rates during the last glacial maximum compared to the Holocene [Bradtmiller *et al.*, 2006; Kienast *et al.*, 2006; Pichat *et al.*, 2004]. This is taken as evidence against SALH. Pichat *et al.* [2004] note that the lower diatom productivity during glacial times "seems to challenge the silicic acid leakage hypothesis." Kienast *et al.* [2006] conclude that the lack of evidence of increased opal burial does "not support silicic leakage hypothesis" during the marine isotope stage 2. Bradtmiller *et al.* [2006] characterize the low glacial opal productivity as "a serious challenge to the SALH," if ocean circulation during the last glacial maximum (LGM) remained similar to the present. This qualification is important, because, as noted by the authors, changes in circulation may have altered the destination of silicic acid leakage such that sedimentary manifestation of SALH would not be obvious in the eastern equatorial Pacific.

[10] In a corollary to SALH, we take a step further to argue that absolute opal accumulation flux in the eastern equatorial Pacific would not necessarily be an adequate or appropriate test of SALH, even if the destination of silicic acid leakage remained the same. This argument rests on the fact that SALH is ultimately a hypothesis that attempts to account for the low glacial atmospheric  $\text{CO}_2$  content by invoking a change in the carbonate pump (i.e.,  $\text{CaCO}_3$ :organic carbon export "rain ratio"). It is not a hypothesis of increased mass flux of silicic acid from the Southern Ocean per se. The leakage is only a means to achieve a reduction in the carbonate pump. A larger absolute flux of the leakage is not always required, because we can envision and demonstrate below that a reduction in the low-latitude carbonate pump can be realized even with a smaller absolute flux of silicic acid leakage, provided that Si:N ratio is elevated in AAIW and SAMW and that the excess Si can be utilized to shift the floral composition in favor of diatoms. It is, in fact, the leakage of waters with elevated Si:N ratios, rather than the leakage of a larger flux of silicic acid, that qualifies more as silicic acid leakage within the context of SALH.

[11] A reduced mass flux of silicic acid with elevated Si:N ratios is possible, if the formation rates of AAIW and SAMW were reduced. Recently, Crosta *et al.* [2007] suggest just such a scenario. They relate benthic foraminiferal  $\delta^{13}\text{C}$  from a subantarctic core raised from 1210 m water depth to AAIW formation rate and the percentage of deep dwelling planktonic foraminifera *G. truncatulinoides* near Tasmania to SAMW formation rate. It will be interesting to see how well this methodology holds up to further scrutiny. In any case, it seems quite possible to us that intermediate water formation rates were different during glacial times when boundary conditions were so different than today.

### 3. Model and Experiment Design

[12] We use the box model of Matsumoto *et al.* [2002], designed originally to examine SALH, to demonstrate its



**Figure 1.** Model of *Matsumoto et al.* [2002] consisting of eight ocean boxes. The original model included a sediment module that allows for open system carbonate compensation, but it is not used in this study.

corollary. The model consists of eight ocean boxes and one well-mixed atmospheric box (Figure 1). The basic concept of the model is the same as the early three-box model of *Toggweiler and Sarmiento* [1985]. Ocean biogeochemistry is chiefly determined by prescribed water fluxes between boxes that represent ocean circulation, export production driven by a single master nutrient restored to some initial values in surface boxes, and air-sea exchange of gases including  $\text{CO}_2$  and  $\text{O}_2$ . The restoring nutrient production is an algorithm, whereby positive deviations of the model nutrient concentration from the observed are reduced toward the observed values. It attributes this reduction to export production. For example, if there is a large supply of nutrient in the model because of upwelling, the diagnosed export production must also be large, so that the model concentration does not become unrealistically high. Nutrients in our model include nitrate, which serves as the master nutrient variable, and silicic acid.

[13] As described in detail by *Matsumoto et al.* [2002], the water fluxes and export production of the (forward) model have been optimized by an inverse model that minimizes the misfit between model predictions and observations of various nutrient concentrations in the ocean and gas concentrations of  $\text{CO}_2$ ,  $^{13}\text{CO}_2$ , and  $^{14}\text{CO}_2$  in the atmosphere. The inverse model approach greatly reduces the arbitrariness involved in traditional hand tuning of box models.

[14] Silica or opal export production ( $\text{Si}_{\text{exp}}$ ) in the model is given as the product of export production based on nitrate ( $N_{\text{exp}}$ ), diatom fraction ( $\text{frac}_{\text{diatoms}}$ ), and Si:N ratio of diatoms being exported ( $\text{Si:N}_{\text{diatoms}}$ ):

$$\text{Si}_{\text{exp}} = N_{\text{exp}} \cdot \text{frac}_{\text{diatoms}} \times \text{Si:N}_{\text{diatoms}} \quad (1)$$

[15] The export production is diagnosed by restoring nitrate to its initial surface values. The fraction of  $N_{\text{exp}}$

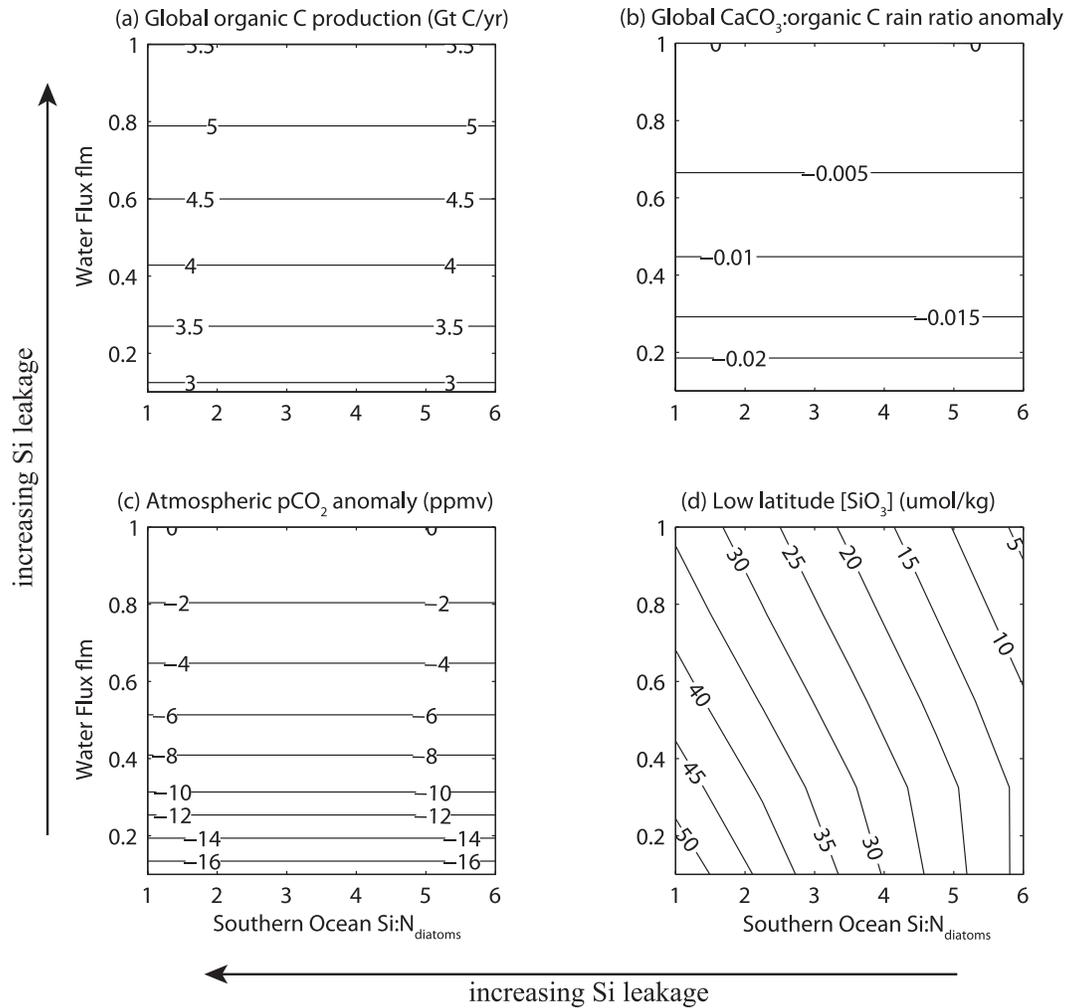
due to diatoms is denoted by  $\text{frac}_{\text{diatoms}}$ . In any single model run, we can either keep  $\text{frac}_{\text{diatoms}}$  constant or allow it to change in response to changes in the availability of silicic acid. For example, we can set  $\text{frac}_{\text{diatoms}}$  to change in order to restore the silicic acid at its initial concentration. On the other hand, if  $\text{frac}_{\text{diatoms}}$  is fixed, an increasing supply of silicic acid will simply result in higher surface concentrations. We assume that diatoms being exported have an elemental stoichiometry that relates silica to nitrogen, given by  $\text{Si:N}_{\text{diatoms}}$ . This ratio is related to Si:N uptake ratio by diatoms, so it is set to lower values when Fe is assumed to be abundant as during glacial times.

[16] Analogously, export production of  $\text{CaCO}_3$  ( $\text{CaCO}_{3,\text{exp}}$ ) is given by

$$\text{CaCO}_{3,\text{exp}} = N_{\text{exp}} \cdot (1 - \text{frac}_{\text{diatoms}}) \cdot (\text{CaCO}_3 : N_{\text{non-diatoms}}) \quad (2)$$

Here  $(1 - \text{frac}_{\text{diatoms}})$  refers to export production by nondiatom phytoplankton, which includes coccolithophorids. The  $\text{CaCO}_3$ :organic carbon rain ratio is determined by the ratio of  $\text{CaCO}_{3,\text{exp}}$  to  $N_{\text{exp}}$ , converted to carbon units. We assume that nondiatom phytoplankton being exported has a ratio that relates inorganic carbon to organic nitrogen, given by  $\text{CaCO}_3 : N_{\text{nondiatoms}}$ . The choice of this ratio is made so that the global  $\text{CaCO}_3$ :organic carbon rain ratio would be about 0.1, a ratio based on our divergence analysis of nutrient data [*Sarmiento et al.*, 2002]. The carbonate pump strength is therefore determined to a large extent by  $\text{frac}_{\text{diatoms}}$ .

[17] Our control run is the “preindustrial state” given in Table 3 of *Matsumoto et al.* [2002]. It is the solution obtained by the inverse model, with  $\text{Si:N}_{\text{diatoms}}$  of the export being 6 in the Southern Ocean surface boxes and 1.5 in the low-latitude surface box. Here  $\text{frac}_{\text{diatoms}}$  is set to 90% in the

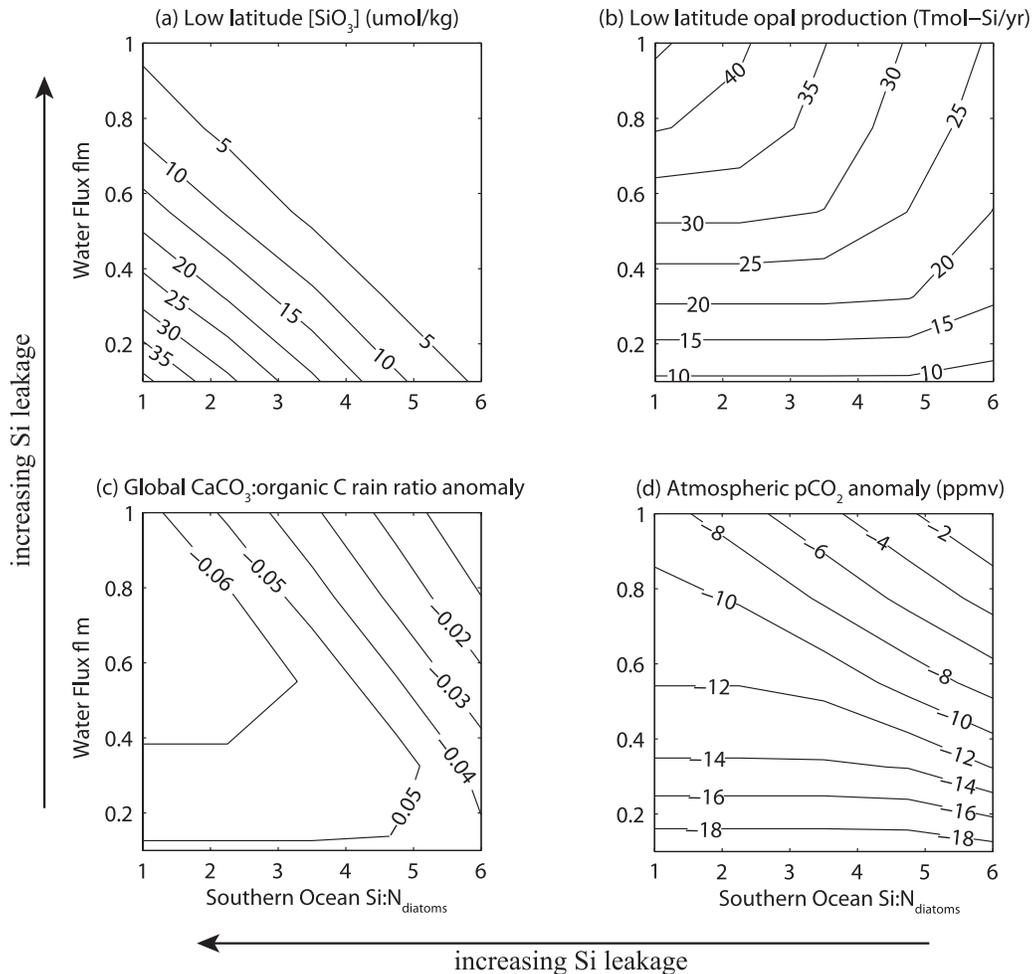


**Figure 2.** Model response to forced changes in Si leakage with no change in low-latitude  $\text{frac}_{\text{diatoms}}$ . The two forcings are fractional changes in water flux flm (vertical axis) and  $\text{Si:N}_{\text{diatoms}}$  in Southern Ocean surface boxes (horizontal axis). Southern Ocean surface  $\text{Si:N}_{\text{diatoms}}$  of 6 represents interglacial, and 1 represents glacial conditions. (a) Global organic carbon export production ( $\text{Gt C a}^{-1}$ ). (b) Anomaly of global  $\text{CaCO}_3$ :organic carbon export rain ratio from control. (c) Anomaly of atmospheric  $p\text{CO}_2$  (ppmv) from control. (d) Silicic acid concentration in low-latitude surface box ( $\mu\text{mol Si kg}^{-1}$ ). Interglacial control is indicated with flm = 1 and  $\text{Si:N}_{\text{diatoms}} = 6$  (top right corner).

two southernmost surface boxes and 50% in the low-latitude surface box.

[18] As illustrated in Figure 1, our model has three boxes in the Southern Ocean that resolve the northward (flux fcp) and southward (fps) transport of upwelled Circumpolar Deep Water. Silicic acid leakage from the Southern Ocean can reach the low-latitude surface box by two routes. One is a surface route that represents cross frontal mixing [Matsumoto *et al.*, 2001] and this occurs via flux fsl. The other is the intermediate water route via flux flm. In the control run, the latter route is quantitatively more significant, because flm (55 Sv;  $\text{Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ) is much larger than fsl (9 Sv) and silicic acid concentration is higher in the middle box representing the intermediate waters ( $16.5 \mu\text{mol kg}^{-1}$ ) than the subantarctic box ( $9.1 \mu\text{mol kg}^{-1}$ ).

[19] We use the model to demonstrate that even a reduced absolute flux of silicic acid leakage can bring about changes predicted by SALH (i.e., smaller carbonate pump and lower atmospheric  $\text{CO}_2$  content), provided Si:N ratio is elevated in intermediate waters and this excess Si can be utilized to the advantage of diatoms over coccolithophorids. This can be simulated in the model by reducing the magnitude of water flux flm. The new model runs add a new dimension to our previous study [Matsumoto *et al.*, 2002], where we demonstrated SALH within the context of changing Southern Ocean  $\text{Si:N}_{\text{diatoms}}$  only. In that study, the  $\text{Si:N}_{\text{diatoms}}$  was reduced from the interglacial value of 6 down to 1 to represent Fe-induced silicic acid underutilization. In this work, we define a new parameter space on the basis of both flm and  $\text{Si:N}_{\text{diatoms}}$ . We seek a steady state response of our model within this parameter space, and so we run the model



**Figure 3.** Model response to forced changes in Si leakage with changes allowed in low-latitude  $\text{frac}_{\text{diatoms}}$  to utilize excess silicic acid. (a) Silicic acid concentration in low-latitude surface box ( $\mu\text{mol Si kg}^{-1}$ ). (b) Opal production in low-latitude surface box ( $\text{Tmol Si a}^{-1}$ ). (c) Anomaly of global  $\text{CaCO}_3$ :organic carbon export rain ratio from control. (d) Anomaly of atmospheric  $p\text{CO}_2$  (ppmv). See Figure 2 caption.

to steady state (1000 years) numerous times for different combinations of the two parameters.

#### 4. Results

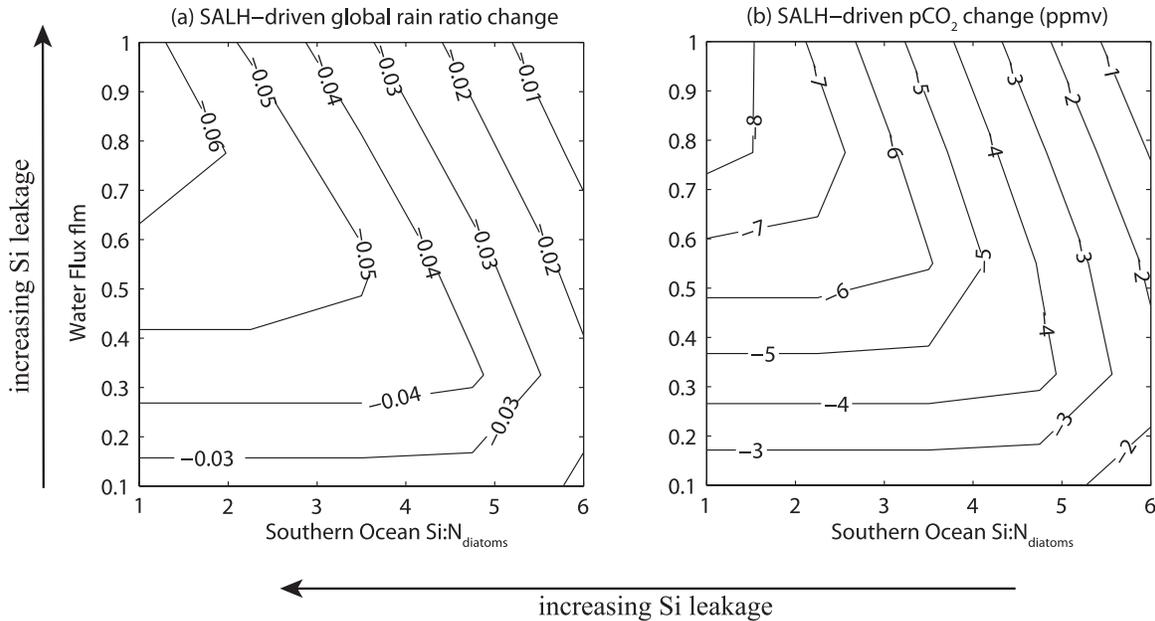
[20] Figure 2 shows the steady state model response within the defined parameter space, while keeping the low-latitude  $\text{frac}_{\text{diatoms}}$  constant. This prevents any shift in the floral composition in response to the excess silicic acid supply relative to nitrate. This restriction is freed in Figure 3. The difference between Figure 3 and Figure 2, shown in Figure 4, allows us to show how the addition of the SALH mechanism affects the  $\text{CaCO}_3$  to organic carbon rain ratio as well as the atmospheric  $\text{CO}_2$ .

[21] A first expectation for a smaller flm is reduction in the upwelling supply of all nutrients to the low-latitude surface box. Deficiency in nitrate causes the global organic carbon production to drop from the interglacial  $5.5 \text{ Gt C a}^{-1}$  to less than  $3 \text{ Gt C a}^{-1}$ , when flm is down to 10% of its original value (Figure 2a). Organic carbon production is

not sensitive to Southern Ocean  $\text{Si:N}_{\text{diatoms}}$ , because it does not affect nitrate. There is a small reduction in the global  $\text{CaCO}_3$ :organic carbon rain ratio with lower flm (Figure 2b), because the drop in global organic carbon production occurs in the low-latitude surface box, which has the lowest  $\text{frac}_{\text{diatoms}}$  and thus highest  $\text{CaCO}_3$ :organic carbon rain ratio. The low-latitude contribution to the global production is thus reduced.

[22] The drop in the  $\text{CaCO}_3$ :organic carbon rain ratio (i.e., reduction in the carbonate pump strength) (Figure 2b) drives down the  $\text{CO}_2$  content in the atmosphere (Figure 2c). The global organic carbon production also drops because of the lower flm, which also the effect of this on atmospheric  $\text{CO}_2$  content is modest, because the preformed nitrate concentrations in surface boxes remain the same because of restoring.

[23] Because  $\text{frac}_{\text{diatoms}}$  is fixed, silicic acid concentration in the low-latitude surface box increases, as both water flux flm and Southern Ocean  $\text{Si:N}_{\text{diatoms}}$  are reduced (Figure 2d).



**Figure 4.** SALH-driven change in (a) global CaCO<sub>3</sub>:organic carbon export rain ratio and (b) atmospheric pCO<sub>2</sub> (ppmv). The difference plots show Figure 3 minus Figure 2.

At first it seems paradoxical that silicic acid concentration should increase with lower flm and thus smaller, absolute silicic acid leakage for a given Si:N<sub>diatoms</sub>. This apparent paradox is explained largely by increased concentration of silicic acid in the subantarctic and middle boxes. The increase in the subantarctic box gives higher input of silicic acid from this box into the low-latitude surface box. The increase in the middle box prevents the input of silicic acid from the thermocline from dropping in direct proportion with the reduction in flm. Because the export of biogenic opal from the surface box is small and remains relatively low in comparison, the only way that the surface low-latitude box can maintain a steady state balance in the face of increased input from the subantarctic, coupled with only a modest decrease in the input from the middle, is to increase its concentration so that the outflowing transport term fsl, fln, and flm, carry more silicic acid out of the surface box. The increases in silicic acid concentration of the subantarctic and middle boxes occur as Si:N<sub>diatoms</sub> in the Southern Ocean surface boxes is reduced (i.e., creates the excess silicic acid) and as flm is reduced (i.e., silicic acid loss via flm is reduced, so the middle box concentration is maintained higher).

[24] In Figure 3, we now allow frac<sub>diatoms</sub> in the low-latitude surface box to change in response to the increased supply of silicic acid, such that the initial silicic acid concentration is restored. Otherwise silicic acid would accumulate (Figure 2d). As shown in Figure 3a, this increased consumption lowers the silicic acid concentration to as low as the initial concentration of about 4 μmol kg<sup>-1</sup>, until frac<sub>diatoms</sub> saturates at 100% in the lower left portion of the diagram, which is expected when silicic acid begins to accumulate (i.e., lower Southern Ocean Si:N<sub>diatoms</sub> increases

silicic acid leakage or smaller flm causes N shortage and therefore reduces export production and silicic acid consumption). Silicic acid concentration over the 5 μmol kg<sup>-1</sup> contour line indicates that no more can be consumed after frac<sub>diatoms</sub> saturates and the flora becomes completely dominated by diatoms.

[25] The changes in frac<sub>diatoms</sub> and silicic acid leakage determine Si<sub>exp</sub> in the low-latitude surface box (Figure 3b). As noted by *Matsumoto et al.* [2002], if circulation is constant but the Southern Ocean Si:N<sub>diatoms</sub> is reduced (i.e., moving to the left along the top of the diagram), then Si<sub>exp</sub> increases from approximately 25 Tmol Si a<sup>-1</sup> (Tmol = 10<sup>12</sup> moles) to 45 Tmol Si a<sup>-1</sup>. However, Si<sub>exp</sub> drops if flm is reduced, and even when Si:N<sub>diatoms</sub> is 1, it is possible to get a Si<sub>exp</sub> smaller than the initial 25 Tmol Si a<sup>-1</sup> by reducing flm to <40% of its original value. For higher Si:N<sub>diatoms</sub>, this threshold is crossed at larger flm.

[26] Figure 3c shows the associated changes in the global carbonate pump, indicated by the global CaCO<sub>3</sub>:organic carbon rain ratio. The changes also include the response to global organic carbon production as in Figure 2b, as the proportions of low-latitude production (high CaCO<sub>3</sub>:organic carbon rain ratio) and high-latitude production (low rain ratio) change. The reduction in the CaCO<sub>3</sub>:organic carbon rain ratio (Figure 3c) largely drives down atmospheric CO<sub>2</sub> content (Figure 3d).

[27] Finally, the differences between simulations with (Figure 3) and without (Figure 2) changes in phytoplankton community composition gives what is realized through SALH (Figure 4). The global carbonate pump strength is reduced, as both Southern Ocean Si:N<sub>diatoms</sub> and water flux flm are reduced (Figure 4a). The difference in atmospheric CO<sub>2</sub> content between Figure 3 and

Figure 2 is driven almost entirely by this weakening of the carbonate pump (Figure 4b).

## 5. Discussion

[28] The atmospheric CO<sub>2</sub> lowering realized by SALH in our model (Figure 4b) is modest for the most part. However, as we reported originally, the “full” impact on atmospheric CO<sub>2</sub> would be much larger for two reasons. First, general circulation models (GCMs) show about 3.5-fold greater sensitivity than box models for the same forcing in low-latitude carbonate pump [Matsumoto *et al.*, 2002]. The large difference in the *p*CO<sub>2</sub> response of box models and GCMs to equivalent forcings is well known and is a subject of much interest [Archer *et al.*, 2000b; Broecker *et al.*, 1999; Toggweiler *et al.*, 2003a, 2003b]. Second, there is an open system, sedimentary carbonate compensation that accompanies the carbonate pump forcing [Matsumoto *et al.*, 2002; Sigman *et al.*, 1998]. At their maximum, the two factors make the responses that we see roughly equivalent to the full 80–100 ppm, glacial-interglacial CO<sub>2</sub> amplitude.

[29] For Southern Ocean Si:N<sub>diatoms</sub> of 1 representing the postulated glacial condition, a 50% reduction in intermediate water flux still causes about a 12 ppm lowering in our box model (Figure 3d). This would amount to more than half of the full 80–100 ppm amplitude, if we consider the two additional factors. In experiments not shown, we have also investigated the model sensitivity to changes in the absolute flux of silicic acid leakage via the surface route (water flux fps) and combination of surface and intermediate water routes (fps and flm). The effect of changing fps is very small.

[30] The validity of our SALH corollary is demonstrated by incremental reductions of the carbonate pump and atmospheric CO<sub>2</sub> content that occur in our model of Figure 3 relative to that of Figure 2 (see Figure 4) despite smaller Si<sub>exp</sub> (Figure 3b). This means that, by themselves, opal accumulation rates in the eastern equatorial Pacific [Bradtmiller *et al.*, 2006; Kienast *et al.*, 2006; Pichat *et al.*, 2004] or any other destination sites of silicic acid leakage provides an insufficient and inconclusive test of SALH. In part, Bradtmiller *et al.* [2006] recognized this and suggest alternative mechanisms, such as a more prevalent El Niño-like condition, that could have upwelled nutrients from different depths and prevented an SALH expression in opal accumulation record even with silicic acid leakage.

[31] Better measures of SALH during glacial times are elevated Si:N ratios in intermediate waters and reduced carbonate pump in low latitudes. In reality, elevated Si:N ratios may not always translate to a shift in floral composition in favor of diatoms, because they can be limited by ecological reasons other than excess silicic acid concentrations and their fraction can saturate (i.e., frac<sub>diatoms</sub> = 100%). Despite this caveat, evaluation of SALH on the basis of these measures paints perhaps a more positive picture of SALH. For example, measurements of sedimentary silicon isotope composition δ<sup>30</sup>Si from the Antarctic and subantarctic indicate reduced silicic acid utilization during glacial times [Beucher *et al.*, 2007; Brzezinski *et*

*al.*, 2002]. If this were driven by increased availability of Fe, then nitrate utilization would likely be higher during the same times. Nitrogen isotope composition δ<sup>15</sup>N on bulk sedimentary organic matter from Antarctic sediments [Franois *et al.*, 1997] and diatom-bound organic matter from Antarctic and subantarctic sediments [Crosta *et al.*, 2005; Robinson *et al.*, 2005; Sigman *et al.*, 1999] support this notion. It should be noted that Fe may not have been the sole cause of silicic acid underutilization and nitrate overutilization, as expanded sea ice coverage or proliferation of nonsiliceous phytoplankton like *Phaeocystis* would have similar effects [Matsumoto *et al.*, 2001].

[32] Perhaps the most direct test of SALH would be the CaCO<sub>3</sub>:organic carbon export rain ratio at the destination sites of silicic acid leakage. To our knowledge there are two paleoceanographic studies that have actually documented this to different degrees. In the first study, Higginson and Altabet [2004] present a record of relative abundance of phytoplankton-specific biomarkers in the Peru margin for the past 20 ka (ka = 1000 years). Their record from 17.5 to 15.5 ka shows higher coccolithophorid:diatom production ratios, coincident with early deglacial rise in *p*CO<sub>2</sub>, may be consistent with SALH. However, other parts of their record are not. As noted by Higginson and Altabet [2004], their record coming from a shallow margin represents an initial test of SALH. It is unclear how representative their data are of the surrounding region.

[33] In the second study, Richaud *et al.* [2007] present a record of <sup>230</sup>Th-normalized, CaCO<sub>3</sub>:organic carbon flux ratio from a sediment core just south of the Galapagos Islands. It shows that the flux ratio is lowest during marine isotope stage 3 and gradually becomes higher toward the present. Romero *et al.* [2003] show a similar trend from the Benguela Upwelling System in the South Atlantic, although their records are not <sup>230</sup>Th normalized and thus not strictly comparable to Richaud *et al.*'s. The variability in Richaud *et al.*'s flux ratio is driven by changes in opal flux, possibly driven by changes in the supply of silicic acid from the Southern Ocean. Their flux ratio therefore appears to reflect shifts in the dominance of diatoms versus coccolithophorids, although the contribution of foraminifera to their CaCO<sub>3</sub> content is not clear. We note that while the impact of changes in the surface alkalinity on atmospheric *p*CO<sub>2</sub> would be the same regardless of whether the alkalinity change is caused by coccolithophorids or foraminifera, SALH calls for a change in the floral composition not faunal composition. In any case, if the Richaud *et al.* record is representative of the region, it would suggest that SALH cannot be the main driver of atmospheric *p*CO<sub>2</sub> change over this period, because Stage 3 with the lowest CaCO<sub>3</sub>:organic carbon flux ratio does not coincide with the time of lowest atmospheric *p*CO<sub>2</sub>. This would be yet another reason to seek multiple mechanisms to explain the glacial-interglacial CO<sub>2</sub> amplitude [Archer, 2004].

## 6. Conclusions

[34] We demonstrated with a simple numerical model that a weakening of the low-latitude carbonate pump within the

framework of SALH requires the availability of excess Si that can be utilized in favor of diatoms over coccolithophorids. SALH does not require a larger absolute flux of silicic acid leakage per se, and such a flux is not necessary to lower atmospheric CO<sub>2</sub> content. This means that opal production and hence accumulation rates in the eastern equatorial Pacific, the most likely destination of silicic acid leakage, should not necessarily increase at times of silicic acid leakage. Recent negative “tests” of SALH based on opal accumulation rates are therefore inconclusive. We suggest that a conclusive test of SALH would need to address the

CaCO<sub>3</sub>:organic carbon export rain ratio, the central SALH prediction and mechanism of CO<sub>2</sub> change.

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